SCIENCE FOR CERAMIC PRODUCTION

CHEMICALLY AND THERMALLY CONJUGATE SYNTHESIS OF SILICON NITRIDE BASED COMPOSITIONS USING FERROSILICON

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The results of synthesis of composite materials based on silicon nitride, which have been discussed from the standpoint of chemical and (or) thermal conjugation, are presented. Synthesis of silicon nitride via the interaction of ferrosilicon in nitrogen in the combustion regime is examined as the inducing process. It is shown that the energy of self-propagating high-temperature synthesis makes it possible to obtain composite, silicon nitride based, ceramic materials in the process of nitriding ferrosilicon: $Si_3N_4 - ZrO_2 - Si_2N_2O$, $Si_3N_4 - TiN - Si_2N_2O$, $Si_3N_4 - BN$, $Si_3Al_3O_3N_5$, and $Si_3N_4 - SiC$.

Key words: silicon nitride, self-propagating and high-temperature synthesis, conjugate processes, nitriding, ferrosilicon, composite ceramic materials.

The principles of chemical conjugation and classical determination of conjugate processes were formulated by N. A. Shilov in 1905 [1]. The term "conjugate reactions" is used "to denote a system of two reactions occurring in the same medium in which one reaction depends in its course on the other." Here "conjugation of reactions is possible only for complex processes which are a sequence of individual reactions and lead to the formation of intermediate products." It should be noted that "purely" chemical conjugation is accomplished under isothermal conditions, when the transfer of chemical energy from a reaction giving to the reaction accepting this energy is possible only in the presence of a common intermediate product.

Thermal or caloric conjugation occurs when in a multicomponent reaction mixture the interaction is maintained with by heat of another, spatially separated, reaction. As a rule, thermal conjugation is used to accomplish synthesis in weakly exothermal systems.

In application to self-propagating high-temperature synthesis (SHS) processes the idea of organization of chemically and thermally conjugate combustion processes is the idea of Academician A. G. Merzhanov [2]. The device now referred to as a "chemical oven" is widely used in the practice of SHS

[3]. Ordinarily, a mixture of powders (Ni + Al, Ti + C, and so on), whose interaction is accompanied by the release of a large amount of heat, are used as the "chemical oven."

In SHS of composite materials, when the initial mix is multicomponent, both thermal and chemical conjugation usually occur. However, to talk about conjugation it is necessary to show that the chemical transformations occur in stages and to determine the role of individual stages in the flow of the process.

The present article presents the results of the synthesis of composite silicon-nitride based materials. These results are discussed from the standpoint of chemical – thermal conjugation.

Nitriding of ferrosilicon in nitrogen gas in a SHS regime is considered as the initiating (primary) process. The basic mechanisms of this process are described in [3, 4]. For the interaction of ferrosilicon with nitrogen in a combustion regime heat is released as a result of the interaction of silicon with nitrogen:

$$3Si + 2N_2 \rightarrow Si_3N_4 + Q.$$
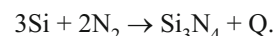
This reaction is so highly exothermal (751 kJ/mole) that the particles of the initial ferrosilicon melt in the heating zone with individual drops of the melt coalescing, which is accompanied by a decrease of the total reaction surface. A consequence of the coalescence process is a low degree of

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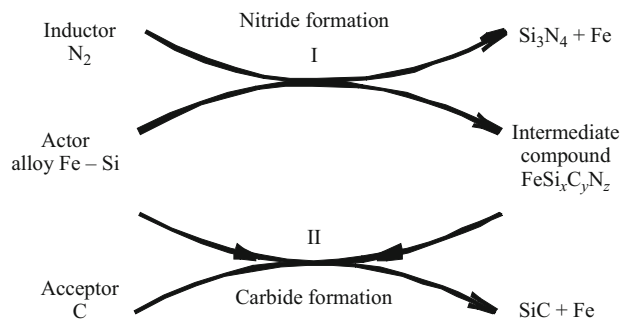
Fig. 1. Conjugation scheme for nitriding and carbide formation processes during the combustion of ferrosilicon in nitrogen.

Fig. 2. Microstructure of ferrosilicon (hardened sample): 1) iron – silicon melt; 2) silicon nitride and carbide border (pressure 4 MPa, sample diameter 50 mm, soot addition 5%).

nitriding of the products of synthesis. To prevent this process, up to 70%[2] of pre-nitrided ferrosilicon is introduced into the initial ferrosilicon. Even with such substantial dilution the maximum combustion temperature reaches 2100°C [5]. The energy store of this system is used to synthesize composite materials, and a corresponding component was introduced into the mix together with or instead of the inert addition (nitride ferrosilicon).

The experiments were performed in a constant-pressure apparatus with nitrogen gas as the atmosphere. The following powders were used to prepare the initial mix: FS 75 ferrosilicon with particles smaller than 160 μm; PM 75 soot; topaz concentrate from the "Kopna" deposit (Kemerovo Oblast) with the composition (%) 40.98 SiO_2, 34.98 Al_2O_3, 2.36 Fe_2O_3, 19.10 (H_2O + F), 1.40 CaO, 1.20 MgO; concentrate from the Tuganskoe deposit (Tomsk Oblast) containing 63.15% ZrO_2 (remainder — silicon dioxide and impurities according to TU U 14-10-015–98); ilmenite from the same deposit, containing 62.10% TiO_2 and the remainder — iron oxide and impurities according to TU-1715-001-58914756–2005; FB 20 commercial ferrosilicon with boron content 20.8%.

The composition Si_3N_4 – SiC finds wide applications in modern technology, since it possesses valuable operational characteristics (high thermal conductivity and heat resistance, chemical resistance in corrosive media, hardness, durability, and other properties) [6 – 8]. A large number of publications are devoted to the synthesis of this composition in the SHS regime using silicon and soot as the initial powders [9, 10]. The combustion of the alloy Fe – Si in the presence of additions of soot has not been studied previously.

A special feature of the alloy studied here is a low melting temperature. As follows from Fe – Si phase diagrams, the temperature at which a liquid phase appears corresponds to the melting temperature of the eutectic $FeSi_2$ – Si (1206°C), which is almost 200°C lower than the melting temperature of silicon (1415°C). In addition, the iron in the alloy catalyzes the nitriding process.

Investigations have shown [11] that in the case of combustion of ferrosilicon without the addition of soot growth of
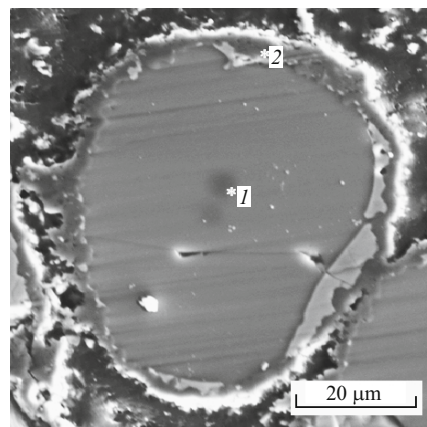
silicon nitride crystals proceeds by two mechanisms: vapor – liquid – crystal (VLC) and via solution — melt crystallization; in addition, the contribution of the latter mechanism is substantial. The eutectic $FeSi_2$ – Si and lebeauite melt in the temperature interval 1206 – 1030°C, and the nitriding process proceeds as a result of the reaction of nitrogen and silicon which is present in the eutectic melt. In addition, silicon evaporates from the eutectic melt and forms silicon nitride in the gas phase via the reaction

$$Si_{(gas)} + N_2 \rightarrow Si_3N_4.$$
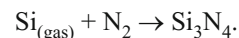
In the presence of soot, when the melting temperature of the eutectic is reached the soot dissolves in the iron – silicon melt with an intermediate compound with variable composition being formed according to the scheme:

$$[Fe – Si]_{melt} + C + N_2 \rightarrow FeSi_xC_yN_z.$$
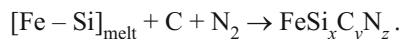
The exothermal process of nitride formation induces the generation of active centers (iron – silicon carbonitride with variable composition). This maintains the reaction in which silicon and carbon interact with one another. The reaction energy of this reaction is small ($\Delta H = – 66.16$ kJ/mole), too small for this process to proceed in a self-maintaining regime.

In Fig. 1 the reagents are denoted in accordance with the terminology adopted for the characteristics of chemically conjugate processes: actor — the substance that participates in both reactions; inductor — the substance which via its interaction with the actor induces a secondary process; acceptor — the substance which accepts the inducing action of the primary reaction; intermediate — an intermediate compound. The iron – silicon carbonitride with the variable composition $FeSi_xC_yN_z$ can be regarded as an intermediate compound which couples two processes — nitriding and carbidizing.

Investigation of the microstructure of hardened samples (Fig. 2) showed that a border consisting of dark and light sec-
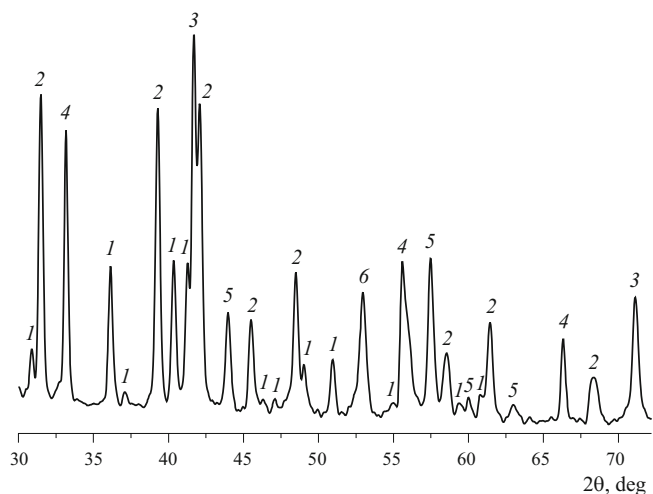
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[2] Here and below — content by weight.

Fig. 3. Fragment of x-ray diffraction pattern of the products of combustion of the mix in nitrogen (ferrosilicon + 10% soot): *1*) α-Si$_3$N$_4$; *2*) β-Si$_3$N$_4$; *3*) SiC; *4*) Si; *5*) FeSi$_2$; *6*) FeSi.

Fig. 4. Electron-microscopic photograph of the products of combustion of ferrosilicon with 10% soot addition in nitrogen.

tions is present on the surface of a melted particle, which x-ray spectral microanalysis shows to consist of a Fe – Si alloy; this suggests that two compounds form on the perimeter of the particle — silicon nitride and carbide.

In turn, the secondary (conjugate) process forming silicon carbide affects the primary process forming silicon nitride, slowing down this process. The result of introducing 10% soot into the initial ferrosilicon is that the heat released as a result of the interaction of silicon with nitrogen is not sufficient for self-propagation of the process and the system loses its combustion capability. XPA of the products of combustion of ferrosilicon with 10% soot added (Fig. 3) established that the intensity of the silicon carbide reflections is higher than that of silicon nitride. The content of silicon and iron disilicide — components of the initial alloy — is substantial, which indicates that the nitride-formation process has not gone to completion. The presence of FeSi, which is a product of dissociation of FeSi$_2$ according to the scheme [12]

$$FeSi_2 \rightarrow FeSi + Fe,$$
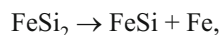
in the products of combustion and absence of iron reflections also attest that the degree of transformation of iron disilicide is low. Even though the energy stores of the system are not used (Si and FeSi$_2$ remain), the combustion process slows down because of the kinetic retardation of the nitride-formation reaction by silicon carbide, formed on the surface of the iron – silicon melt. The combustion temperature decreases; this is indicated by the appearance of the low-temperature α-modification of Si$_3$N$_4$, which transforms into β-Si$_3$N$_4$ at a temperature of about 1450°C, in the products of combustion.

The results of the scanning-electron-microscopic investigations showed that silicon nitride and carbide are present as grains in the products of combustion (Fig. 4), while whisker crystals, which are characteristic for both compounds, were
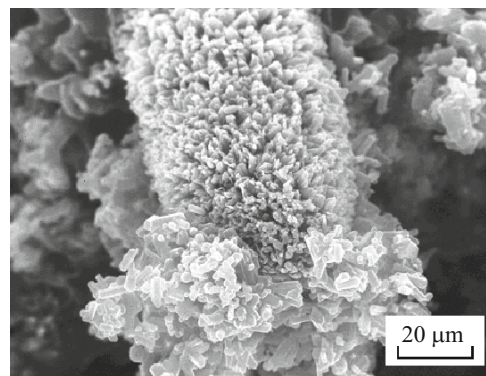
not observed. This shows that the reaction proceeds mainly by the liquid – gas mechanism and not via the vapor-gas phase by the VLC mechanism. The realization of the gas-phase mechanism is possible at synthesis temperatures 1500°C, when the equilibrium silicon vapor pressure is already substantial [13] and self-evaporation of silicon particles smaller than 10 μm is possible [14]. Kinetic retardation of the nitride-formation reaction by the layer of product is observed in the presence of soot; the combustion process proceeds at relatively low temperatures (about 1500°C), which is reflected in the form and sizes of the crystals.

It should be noted that soot as a refractory component of the system (sublimation temperature 3700°C) should improve the conditions of nitrogen filtration to the reaction zone as a result of the prevention of coagulation of melted particles of ferrosilicon. This same effect can be attained by diluting the initial mix with a product of combustion, for example SiC (decomposition temperature 2830°C). The main difference between these components is that the carbon is a chemically active reagent, and silicon carbide is an inert diluent. The experiments showed (Fig. 5) that introducing SiC substantially increases the limits of stable combustion of the system (50% SiC instead of 10% C) and the degree of nitriding of the products of synthesis increases. The results of this experiment likewise show that it is the silicon carbide formation reaction that affects the parameters of the nitriding process.

On the whole one can say that there is a mutual "intensification – attenuation" of the reactions or "chemical intensification" — decrease of the rate of formation of the products of the primary reaction and acceleration of the formation of the products of the secondary reaction; this is confirmed by the results of XPA analysis of the products of combustion (see Fig. 3). It is evident that the intensity of silicon carbide reflections is comparable to that of silicon nitride reflections; the soot addition to the ferrosilicon is only 10%.

The creation of conditions for which a balance is possible between the rates of the two processes (nitride and carbide formation) makes possible synthesis of the composition Si$_3$N$_4$ – SiC in a self-propagating regime.
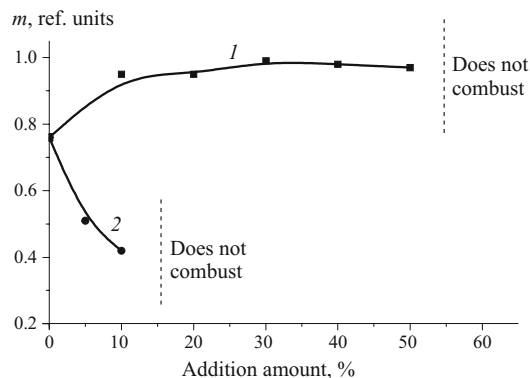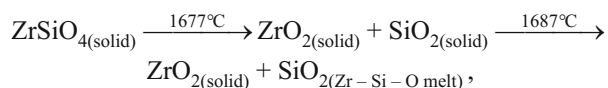
Fig. 5. Degree m of nitriding of the products of combustion of ferrosilicon in nitrogen versus the silicon carbide (1) and soot (2) addition amounts; nitrogen pressure 4 MPa, sample diameter 50 mm.

During the combustion of ferrosilicon in the presence of zircon additions the heat released from the interaction reaction between silicon and nitrogen induces an endothermal process of zircon dissociation, which proceeds according to the scheme [15]

$$ZrSiO_{4(solid)} \xrightarrow{1677°C} ZrO_{2(solid)} + SiO_{2(solid)} \xrightarrow{1687°C}$$
$$ZrO_{2(solid)} + SiO_{2(Zr-Si-O\ melt)},$$

with the formation of zirconium dioxide and high-silica zirconium-silicate melt. It is known [16] that the following reaction proceeds at temperatures above 1200°C:

$$SiO_{2(solid)} + Si_{(solid)} \rightarrow SiO_{(gas)}.$$
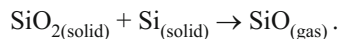
In the SHS process, gaseous silicon monoxide is released in the interaction of SiO_2 with iron – silicon melt according to the scheme

$$SiO_{2(Zr-Si-O\ melt)} + Si_{(Fe-Si\ melt)} \rightarrow SiO_{(gas)},$$
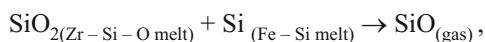
The silicon monoxide is nitrided in the gas phase and condenses in the form of silicon oxynitride Si_2N_2O in the colder (outer) part of the sample. The products of the conjugate process in this case are zirconium dioxide and silicon oxynitride.

It should be noted that commercial technologies for reprocessing zirconium concentrate for the purpose of obtaining zirconium dioxide are complex and energy-intensive, since zircon is one of the most stable and most refractory minerals. The chemical inertness of zircon is due to its structure, where silicon-oxygen and zirconium-oxygen tetrahedra alternate. The accomplishment of chemothermal conjugation made it possible to obtain a composite ceramic material $Si_3N_4 - ZrO_2 - Si_2N_2O$ only as a result of the energy of chemical transformation.

In the presence of additions of a topaz concentrate, the propagation of a reaction wave of combustion also occurs as a result of the interaction of silicon and nitrogen. Ahead of the combustion front the topaz is subjected to thermal destruction with formation of mullite $3Al_2O_3 \cdot 2SiO_2$ and silica in the form of cristobalite and gaseous hydrogen fluoride [17]:

$$6[Al_2SiO_4(F,\ OH)_2] \rightarrow 2[3Al_2O_3 \cdot 2SiO_2] + 2SiO_2 + 6HF.$$

The following reaction is probable at temperatures above 1000°C:

$$SiO_2 + 4HF \rightarrow SiF_4\uparrow + H_2O\uparrow.$$
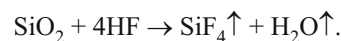
As temperature increases above 1800°C the mullite melts and decomposes with corundum (Al_2O_3) being released; the latter dissolves in the crystal lattice of silicon nitride, forming β-sialon with the composition $Si_3Al_3O_3N_5$. This is confirmed by the XPA data for the products of nitriding.

The ceramic composition $Si_3N_4 - TiN - Si_2N_2O$ was synthesized by introducing ilmenite concentrate into ferrosilicon. Ilmenite, or titaniferous iron ore, is a mineral belonging to the subclass of complex oxides with the formula $FeTiO_3$ ($FeO \cdot TiO_2$). When ilmenite concentrate is added to ferrosilicon the process of nitriding ferrosilicon induces the process of reduction of titanium and iron oxides by silicon. The reduction of TiO_2 to titanium by silicon according to the reaction

$$TiO_2 + Si = Ti + SiO_2$$
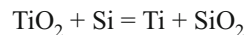
is thermodynamically impossible according to the isobaric-isothermal potential of this reaction [18]:

$$\Delta G_T^0 = -256 + 18.96T.$$

However, this reaction can proceed with iron present in the mix even with a high concentration of silicon. Under these conditions the reduction of titanium dioxide proceeds in steps according to the reactions:

$$2TiO_2 + Si = 2TiO + SiO_2;$$

$$2TiO + Si = 2Ti + SiO_2.$$
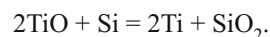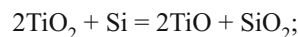
Simultaneously, reduction of iron oxide occurs in the reaction wave of combustion:

$$2FeO + Si = 2Fe + SiO_2.$$
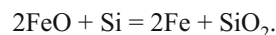
Iron forms intermetallic compounds with titanium and thereby facilitates the reduction of titanium oxide to titanium. In a nitrogen gas atmosphere, nitriding of ferrotitanium and silicon dioxide occurs with formation of titanium nitride and silicon oxynitride (Fig. 6).

The composition $Si_3N_4 - BN$ was synthesized with the participation of iron – boron alloy. It was not possible to organize self-sustaining combustion of ferroboron in nitrogen in the SHS regime because the content of nitride-forming element was inadequate for self-propagation of the process.
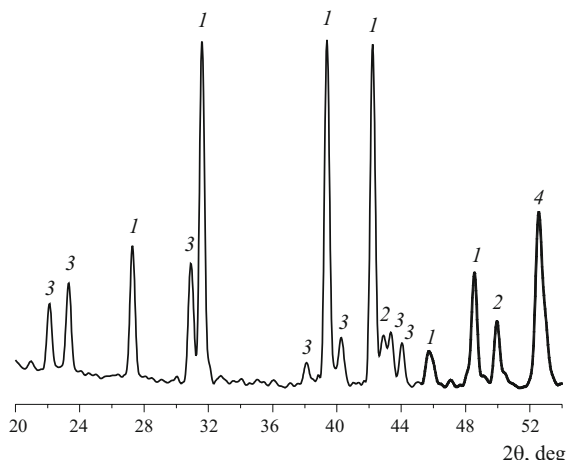
Fig. 6. Fragment of an x-ray diffraction pattern of the product of combustion of the mix 48% ferrosilicon + 20% ilmenite + 32% nitride ferrosilicon: 1) β-Si_3N_4; 2) TiN; 3) Si_2N_2O; 4) Fe.

When ferroboron is added to ferrosilicon, the process of nitriding of the latter proceeded by means of thermal conjugation. The combustion process was observed with up to 50% Fe – B addition. According to the XPA results, the products of combustion consisted of the β modification of silicon nitride, hexagonal modification of boron nitride, and α-iron.

Acid enrichment made it possible to obtain high-purity ceramic compositions in all iron systems.

In summary, chemical and (or) thermal conjugation play the leading role in the processes of SHS of composite materials based on silicon nitride. It was shown that the heat of a "high-temperature chemical reactor" (the interaction reaction between ferrosilicon and nitrogen) can be used to synthesize the ceramic compositions Si_3N_4 – SiC, Si_3N_4 – ZrO_2 – Si_2N_2O, Si_3N_4 – SiN – Si_2N_2O, and Si_3N_4 – BN.

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